NISI MONOGRAPHS

CHEMISTRY OF BI- AND TRIPOSITIVE SILVER

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SILVER JUBILEE ISSUE

1960

National Institute of Sciences of India

PREFACE

Silver in its higher oxidation states may be said to have been the subject of study from more than a century and half ago, though no serious attention was paid to the problem till towards the close of the nineteenth century, Since then, however, there has accumulated a more or less voluminous literature on the subject of a rather limited character and some facts of highly interesting and exciting nature have been revealed now and then from researches in the field of coordination complexes. Barring one or two short reviews there has been no attempt to furnish a systematic and comprehensive account of the subject till now. That such an account will be of considerable use to the workers in this line needs little emphasis to state here, as the results already achieved promise a richer harvest in future.

We have, therefore, taken advantage of this occasion of celebrating the Silver Jubilee of the National Institute of Sciences of India to prepare the present monograph on the subject with the hope that it might fulfil the need felt by those engaged in researches on the chemistry of silver in its unusual valency states.

Our best thanks are due to Dr. Supriya Roy for the microphotographs included in this work.

PREFACE

Silver in its higher oxidation states may be said to have been the subject of study from more than a century and half ago, though no serious attention was paid to the problem till towards the close of the nineteenth century, Since then, however, there has accumulated a more or less voluminous literature on the subject of a rather limited character and some facts of highly interesting and exciting nature have been revealed now and then from researches in the field of coordination complexes. Barring one or two short reviews there has been no attempt to furnish a systematic and comprehensive account of the subject till now. That such an account will be of considerable use to the workers in this line needs little emphasis to state here, as the results already achieved promise a richer harvest in future.

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ERRATA

1. In line 4 of the Preface after century *for* , *read* .
2. P. 1, paragraph 2 in line 3, *for* $(n-1)d^{10}s^2$ *read* $(n-1)d^{10}ns^1$.
   „ paragraph 2 in line 4, *for* 3, 4 and 5 *read* 4, 5 and 6.
3. P. 5, in line 3 from the bottom for (x_1-x_2) *read* (x_2-x_1).
4. P. 22, in line 9 *for* oxidiing *read* oxidizing.
5. P. 32, reference No. 21, for Noyts *read* Noyes.

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CHEMISTRY OF BI- AND TRIPOSITIVE SILVER

INTRODUCTION

Silver, an element of the second transition series, shows normally a positive valency of 1 in keeping with its position in Group I, Subgroup B, of Mendeleef's Periodic Table. But there are compounds where it is known to occur with a higher positive valency of 2, which is the common oxidation state of its lower homologue copper in the same subgroup. Compounds are also known in which silver manifests a still higher valency of 3, so characteristic of its higher homologue gold. These higher oxidation states of silver are particularly stabilized, as in the case of many other elements, by complex formation; for, the tendency of Ag^{2+} and Ag^{3+} to resume the normal state of Ag^{+} by capture of one or two electrons is opposed by the screening effect of an envelope of negative charges from the polar coordinating ligands.

The chemical analogy of silver with copper and gold in the same subgroup rests obviously on their having the same configuration of the outermost electrons, $(n-1)d^{10}s^2$, and the same ^2S ground state. The value of n for copper, silver and gold is given respectively by 3, 4 and 5. A comparison of their ionization and electrode potentials reveals the relative stability of their ions in the different states of valency as shown below.

	Cu	Ag	Au
Ionization potential $I(1)-(eV)$	7.72	7.87	9.22
E^0 M/M^+ (V)	0.522	0.799	1.68
M/M^{2+} „	0.345	1.390	
M/M^{3+} „			1.42
M^+/M^{2+} „	-1.70	2.0	

The electrode potential values indicate that the silver ions should become increasingly unstable with increasing charge, showing an increasing tendency for reduction, and that the reverse would hold good for copper and gold. This is supported by observed facts. For, while unipositive silver compounds are quite stable and compounds of bi- and tripositive silver are easily reduced, those of bipositive copper and tripositive gold are much more stable than their corresponding unipositive compounds. This is accounted for by the fact that the heat of hydration for Cu^{2+} compared with that for Cu^+ makes the cupric compounds in aqueous solution more stable, in spite of the quite high second ionization energy (20.2 eV) of copper. It is well known that cuprous compounds in aqueous solution suffer an easy disproportionation into metallic copper and cupric compounds:

$$2Cu^+ \text{ (aq)} \longrightarrow Cu + Cu^{2+}\text{(aq)}.$$

This differs strikingly from the behaviour of Ag^+ ion. Unipositive gold also behaves like copper in this respect:

$$3Au^+ \text{ (aq)} \longrightarrow 2Au + Au^{3+} \text{ (aq)}.$$

A comparison of the equilibrium constant of the cupric (II)—cuprous(I) system with that of the argentic (II)—argentous (I) system reveals this difference quite clearly.

$$\frac{[Cu^{2+}]}{[Cu^+]^2} = 1.2 \times 10^6 ; \quad \frac{[Ag^{2+}]}{[Ag^+]^2} = 10^{-20} \text{ at } 25°C.$$

In complex formation both copper and silver can occur in the tripositive state; but curiously enough the compounds of tripositive silver are more stable than those of tripositive copper, though there is not much difference between the two elements in their second and third ionization potentials. Thus while in the case of copper the stability of its valency states follows the order bi- > uni- > trivalent, that in the case of silver is given by uni- > bi- and trivalent. Then again for the same valency state the stability order for the two elements can be represented as Ag(I) > Cu(I), Cu(II) > Ag(II), and Ag(III) > Cu(III). Another interesting observation made in this connection is the phenomenon of direct oxidation of Ag(I) to Ag(III) in many cases without the intermediate formation of Ag(II), which is then formed from Ag(III) by subsequent reduction (Noyes *et al.* 1935). The disproportionation of Ag(II) into Ag(III) and Ag(I), demonstrated by some workers (Barbieri 1931; Gordon and Wahl 1958), is presumably related to it. In the case of gold the bipositive state is practically unknown. The difference, thus exhibited by silver in its different oxidation states from its lower and higher homologues copper and gold in spite of similar electronic configurations (viz. d^{10} for uni-, d^9 for bi- and d^8 for tripositive state), is rather intriguing.

In the present work we propose, therefore, to make a comprehensive and critical treatment of the chemistry of bi- and tripositive silver in which we have been interested for several years.

Reference may also be made here to a short but excellent review on the subject by Bailar (1944) that appeared in the Journal of Chemical Education nearly 16 year ago. A short, but very informative, chapter on the subject has also been included by Kleinberg (1950) in his book on the "Unfamiliar Oxidation States and their Stabilization".

I. SIMPLE COMPOUNDS

(a) Oxides of Silver(II) and Silver(III); Silver Peroxysalts.

As early as in 1804 Ritter obtained a black crystalline powder that separated at the anode when an electric current was passed between platinum electrodes through an aqueous solution of silver nitrate. The substance was for a long time considered to be a peroxide of silver, as it was found to give off oxygen when heated. Subsequent analyses of the product by various workers (Mulder and Heringa 1896; Mulder 1897, 1898, 1903; Sulc 1896, 1900; Tanatar 1901; Watson 1906; Barbieri 1906, 1907) almost after a century revealed the presence of nitrogen in the compound with a composition represented by the formula, Ag_7NO_{11} or $3Ag_2O_2.AgNO_3.2O$. The name silver peroxynitrate was generally given to it. This was formulated as $2Ag_3O_4.AgNO_3$ by Tanatar (1901). By the eletrolysis of solutions of other salts of silver, or of acids with a silver anode, peroxysulphate of the composition, $5Ag_2O_2.2Ag_2SO_7$ (Mulder 1900), and the peroxyfluorides, $Ag_{15}F_3O_{16}$ or $4Ag_3O_4.3AgF$ and Ag_7FO_8 or $2Ag_3O_4.AgF$ (Tanatar 1901), were obtained. The black crust, which was observed by Schiel (1864) to separate on a silver anode during the electrolysis of dilute sulphuric acid, was very probably this peroxysulphate and not silver peroxide or dioxide.

Wöhler (1867) had described the preparation of a silver dioxide by the action of ozone on silver monoxide or silver, and an oxide of the composition, Ag_4O_3, was believed by Berthelot (1880) to result from the action of alkaline H_2O_2 on silver nitrate solution. Marshall (1900), as also Marshall and Inglis (1902), reported the formation of silver peroxide as a black precipitate by the action of potassium persulphate on silver nitrate or silver sulphate solution. The decomposition of silver peroxynitrate with boiling water was found to give oxygen and silver nitrate with separation of silver peroxide (Mulder 1898; Watson 1906) according to the equation:

$$Ag_7NO_{11} = 3Ag_2O_2 + AgNO_3 + O_2.$$

The peroxide, Ag_2O_2, reacts with ammonia, oxidizing the latter to nitrogen (Watson 1906):

$$6Ag_2O_2 + 2NH_3 = 3Ag_4O_3 + N_2 + 3H_2O.$$

The oxide, Ag_4O_3, has, however, not been isolated.

That these oxidation products of silver are not true peroxides, but a compound or a mixture of compounds of silver in a higher oxidation state, was demonstrated by Barbieri (1906, 1907). For, an acid solution of these oxidation products was found by him not to be affected by permanganate, manganese dioxide or lead peroxide, contrary to peroxy compounds. Moreover, they were not found to give any hydrogen peroxide on treatment with acids as could be proved by titanium test (Yost 1926). The black precipitate formed by the action of potassium persulphate on silver nitrate solution was, however, found to consist of a mixture of $Ag_2S_2O_8$ and Ag_2O_2 (Austin 1911).

Luther and Pokorny (1908) have shown that in alkaline solution silver or Ag^+ is reversibly and quantitatively converted by anodic oxidation only to the bipositive, Ag^{2+}, state, while in acid solution the oxidation goes up to the tripositive, Ag^{3+}, state. They measured the oxidation potentials of the systems $AgO-Ag_2O$, and of Ag_2O_3-AgO, as well as of $Ag_2O_3-Ag_2SO_4$ (saturated). Their results have been confirmed by many subsequent workers (Baborovsky and Kuzma 1909; Brown 1916; Jirsa *et al.* 1926; Barbieri 1931; Carman 1934). Silver peroxynitrate, when reduced in 1*N* NaOH, shows an indication of the existence of tripositive silver. Luther and Pokorny (1908) observed three different potentials of 1·57 volts, 1·41 volts and 1·17 volts. The last two corresponded to the known values for the change of $AgO \longrightarrow Ag_2O$ and $Ag_2O \longrightarrow Ag$ states respectively. The higher value of 1·57 volts was, therefore, considered to correspond to a reduction from a still higher state, and in all probability from Ag_2O_3 to AgO. They have further found that in acid solution the compound Ag_2O_3 is directly decomposed into Ag on electrolytic reduction and conversely Ag can be oxidized directly to Ag_2O_3. A potential of 1·74 volt has been recorded by them for the E.M.F. of the cell

$$Pt(Ag_2O_3,\ Ag_2SO_4 sat.) \parallel 0.5N\ H_2SO_4,\ H_2$$

From a determination of the transference number of silver in a solution of AgO in nitric acid Weber (1917) concluded that at least a portion of the oxide should be considered as an oxide of tripositive silver.

The formation of silver(III) by the action of dry ozone on dry pulverized silver was established from potential measurement by Jisra *et al.* (1926). The product thus obtained was not pure Ag_2O_3, but a solid solution of Ag_2O_3, Ag_2O_2 and Ag_2O, their relative proportions depending on the condition for oxidation.

The marked catalytic effect of Ag^+ ion in certain oxidations by persulphate is attributed to the formation of an unstable oxide, Ag_3O_4 (Higson 1921), or of the unstable Ag^{3+} ion (Yost 1926; Yost and Claussen 1931; Bekier and Kijowski 1934; Dekker, Levy and Yost 1937). The mechanism of this catalytic oxidation, for instance in the case of Cr(III) to Cr(VI), is represented as follows:

$$Ag^+ + S_2O_8^{2-} \qquad\qquad + 2SO_4^{2} \text{ (slow)},$$
$$3Ag^{3+} + 2Cr^{3+} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 3Ag^+ + 14H^+ \text{ (rapid)}.$$

Malaguti (1952), on the other hand, attributes this catalytic effect to the Ag^{2+} ion in contradiction to Yost's view. He has shown that *bis*-$\alpha\alpha'$-dipyridyl silver(I) ion, which is oxidized by persulphate to the corresponding complex of silver(II) ion, is as effective a catalyst as Ag^+ ion. A similar view has been advanced by Bawn and Margerison (1955). It might, however, be argued that it is not Ag^{2+} ion but Ag^{3+} ion, arising out of dismutation of Ag^{2+} into Ag^+ and Ag^{3+}, which actually acts as the catalyst here (cf. Barbieri 1931).

The black precipitate formed by the action of persulphate on silver nitrate solution, when rapidly analysed, shows the presence of silver in the tripositive state in the product (Yost 1926; Carman 1934), and the substance was believed to be either Ag_2O_3 or a basic Ag(III) sulphate (Yost 1925). On standing, it loses oxygen and changes ultimately to a product containing Ag(III) and Ag(II) in equal amounts (Carman 1934).

Many chemical and physical properties of silver(II) oxide were studied by Jirsa (1925).

On treatment with sulphuric or perchloric acid the compound dissolves at first to form a brown solution, but decomposes readily to liberate all its active oxygen quantitatively:

$$2Ag_2O_2 + 2H_2SO_4 \longrightarrow O_2 + 2Ag_2SO_4 + 2H_2O.$$

It is a powerful oxidizing agent which can liberate nitrogen from ammonia solution. Hydrazine hydrate is quantitatively oxidized by it with evolution of nitrogen and formation of metallic silver:

$$Ag_2O_2 + N_2H_4.H_2O \longrightarrow N_2 + 2Ag + 3H_2O.$$

When dissolved in nitric acid silver(II) oxide yields a brown solution of high oxidizing power with partial decomposition into silver(I) and with liberation of oxygen. The extent of decomposition increases with temperature and dilution of the acid. From the brown solution in strong nitric acid it can be reprecipitated by dilution with water (Jirsa 1925). Similar observations were made also by Carman (1934).

The same author (Jirsa 1925) determined the heat of reaction of silver (II) oxide with perchloric acid, hydrazine hydrate and nitric acid respectively by calorimetric measurement. Similar measurements were made for the oxide, Ag_2O, as well. As the reaction of the two oxides with these reagents in dilute solution is rather slow, the measurements were made in their concentrated solutions and the values obtained were extrapolated to zero dilution in each case. The difference between the zero-dilution values of the two oxides in each case was found to be 1,000 cal. nearly.

$$Ag_2O_2 + 2HClO_4 \longrightarrow 2AgClO_4 + H_2O + \tfrac{1}{2}O_2 + x_2 \text{ cal.}$$
$$Ag_2O + 2HClO_4 \longrightarrow 2AgClO_4 + H_2O + x_1 \text{ cal.}$$
$$(x_1 - x_2) = (10{,}964 - 9{,}964) = 1{,}000 \text{ cal. approx.}$$

This gives the heat of formation of Ag_2O_2 from Ag_2O:
$Ag_2O_2 \longrightarrow Ag_2O + \tfrac{1}{2}O_2 + 1{,}000$ cal. Taking the value of the heat of

formation of Ag_2O as 6,440 cal. (Lewis) the heat of formation of Ag_2O_2 from silver and oxygen was given by the author (Jirsa 1925) as 5,440 cal.; i.e. $Ag_2O_2 \longrightarrow 2Ag + O_2 - 5{,}440$ cal. The necessity of extrapolation, however, introduces some amount of uncertainty in the heat values calculated. From these values of heat of formation of Ag_2O_2 from Ag_2O and from Ag the author calculated by means of approx. Nernst formula the dissociation pressures of Ag_2O_2 into Ag_2O and into Ag as $3{\cdot}96 \times 10^8$ and $1{\cdot}37 \times 10^3$ atm. respectively at 25°C.:

$$\log p_{O_2} = -Q/4{\cdot}571\ T + 1{\cdot}75 \log T + 2{\cdot}8.$$

In spite of these high values of dissociation pressure the existence of Ag_2O_2 in the thermodynamic sense at room temperature in a fairly stable condition must be attributed to some passivity phenomenon (Jirsa 1925).

The physicochemical investigations, however, demonstrate the existence of bipositive silver more precisely than the tripositive one. Luther and Pokorny (1908) have shown that the voltage-current curve for a silver anode in sodium hydroxide solution shows that the silver is quantitatively oxidized first to Ag_2O and then to AgO. Under these experimental conditions there is no indication of the formation of tripositive silver ion.

The oxidation of silver in nitric acid solution with ozone was extensively studied by Noyes *et al.* (1935). The oxidation leading to the formation of a black soluble argentic nitrate was found to reach an incomplete but steady state due to the reduction of the product by water with evolution of oxygen. From a study of the rate of oxidation at 0°C the authors assumed the intermediate formation of an oxygenated tripositive silver ion:

$$Ag^+ + O_3 = AgO^+ + O_2 \text{ (slow)},$$
$$AgO^+ + Ag^+ + 2H^+ = 2Ag^{2+} + H_2O \text{ (fast)}.$$

By oxidimetric titration and magnetic measurements they, however, proved that in the steady state the silver was present completely in the bipositive form in solution. To account for the precipitation of basic salts of silver (III) from the latter on dilution the authors proposed the following equilibrium reaction:

$$2Ag^{2+} + H_2O \rightleftharpoons Ag^+ + AgO^+ + 2H^+.$$

The standard oxidation potential for the system $Ag^{2+} - Ag^+$ was determined by Noyes and Kossiakoff (1935) from the measurement of E.M.F. between platinum electrodes of silver(I) and silver(II) nitrates in 1-2*N* HNO_3 against hydrogen electrode. The value was found to be 1.914 ± 0.002 volts. This is, however, much higher than 1.41 volts reported earlier by Luther and Pokorny (1908), as well as by others, from determination in alkaline solution. This higher value of 1.914 volts for the standard oxidation potential of the system $Ag^{2+} - Ag^+$ in acid solution is regarded as a support to the hypothesis that the decomposition of bipositive silver by water with evolution of oxygen proceeds through the intermediate formation of hydrogen peroxide; because the potential for the reaction,

$$H_2O_2 + 2H^+ + 2e = 2H_2O,$$

has a value of only 1.77 volts.

The rate of reduction by water of silver(II) nitrate in nitric acid solution of various acid concentrations has been studied at 0° and 25°C by Noyes, Coryell et *al.* (1937). The rate of reduction for the overall reaction,

$$4Ag^{2+} + 2H_2O \longrightarrow 4Ag^+ + 4H^+ + O_2,$$

is represented by the equation,

$$\frac{-d(Ag^{2+})}{dt} = k_2 \frac{(Ag^{2+})^2}{(Ag^+)} + k_4 \frac{(Ag^{2+})^4}{(Ag^+)},$$

where both k_2 and k_4 decreased greatly with increase in the concentration of nitric acid. The equation was derived by assuming the occurrence of two independent reactions, both involving the presence of tripositive silver in equilibrium with uni- and bipositive species.

The standard oxidation potential in 4*N* $HClO_4$ at 25°C for the reaction, $Ag^{2+} + e = Ag^+$, was found to have a value of 2.0 volts (Noyes, Devault *et al.* 1937). This is about 66-71 millivolts higher than that found in 4*N* HNO_3 solution. While the silver(II) nitrate solution in nitric acid was found to be coloured black to brown, silver(II) perchlorate in perchloric acid solution (60 per cent or below) is, on the other hand, pink. The above observations have been explained by the assumption that in nitric acid solution the bipositive silver mainly exists in the form of a nitrate complex, because the solubility of Ag(II) increases with the concentration of NO_3^- ion at a constant hydrogen ion concentration. The passage of some silver to the anode during transference experiment in the dark brown solutions obtained by dissolving silver(II) oxynitrate in concentrated nitric acid is also in support of the above assumption that bipositive silver in concentrated nitric acid exists mainly in the form of a nitrate complex (Weber 1917). Silver(II) oxide, AgO, is converted in 3*N* HNO_3 into silver(II) oxynitrate after equilibrium is attained. The empirical composition of the product corresponded to the formula, $AgO_{1.48} (NO_3)_{0.153}$. A more or less similar product was obtained by electrolysis by earlier workers.

By the electrolysis of $AgClO_4$ in perchloric acid solution the precipitate of an unstable oxide or a basic salt of tripositive silver was said to be produced. This substance appeared also to be formed on the surface of AgO, when the latter was treated with perchloric acid (Noyes, Devault *et al.* 1937).

From the standard oxidation potentials measured at 0°C and 25°C, Noyes, Devault *et al.* (1937) calculated the thermodynamic constants for the reactions in the cells:

(i) Pt (H_2, H^+) ‖ (Ag^{2+}, Ag^+ (4*M* HNO_3))

(ii) Pt (H_2, H^+) ‖ (Ag^{2+}, Ag^+ (4*M* $HClO_4$))

The values obtained are: (i) $\Delta F^\circ = -44.49$ kcal.; $\Delta H^0 = -41.0$ kcal. (ii) $\Delta F^\circ = -46.13$ kcal.; $\Delta H^0 = -41.1$ kcal.

Silver (II) oxide, AgO, has also been prepared by other methods besides the hydrolysis of silver peroxynitrate. Lustrous black crystals of the compound were obtained by passing fluorine into a cold solution of $AgNO_3$ or $AgClO_4$ or of AgF in a platinum tube (Fichter and Goldach 1930). Jirsa (1947, 1949) prepared it by adding an alkaline solution of potassium persulphate to a boiling solution of silver nitrate (cf. DeBoer and Ormondt 1952).

Sen (1948) has shown that values for certain physical constants of silver like entropy, vibration frequency, the distance of closest approach of atoms, and others calculated on the basis of the bivalency of silver are in good agreement with their observed values.

Kappana and Talaty (1951) have shown that in the electrolysis of silver fluoride solution the decomposition potential curves ran parallel to the current-anode potential curve, each exhibiting two breaks; while the current-cathode potential curve gave only one break. The second break in the decomposition potential curves is said to be associated with the anodic deposition of a black crystalline compound as reported by Tanatar (1901). But they found no fluorine in the product and represented it, on the basis of its silver content, as an oxide of tetrapositive silver having the composition AgO_2. There is, however, no justification for this assumption in view of the absence of any analytical result for the oxidation state of silver or for the peroxidic oxygen in the compound. It seems quite probable that the product is a mere hydrated higher oxide of silver, $Ag_3O_4.2H_2O$, as the authors did not take proper care to dry the product before analysis. The determination of the silver content of the substance was based on the analysis of moist specimens only. The substance was also found to be feebly paramagnetic with a moment value of 0.37 B.M. only.

The anodic behaviour of silver in 2*N* H_2SO_4 at 25°C was studied by Jones and Thirsk (1954). The oxidation was found to occur as $Ag \longrightarrow Ag_2SO_4 \longrightarrow AgO + O_2(g)$, and the reduction of the oxidized anode to follow the sequence $AgO \longrightarrow Ag_2SO_4 \longrightarrow Ag + H_2(g)$. An X-ray analysis of the oxide formed at the anode demonstrated its identity with specimens of AgO prepared by chemical methods, though admixed with traces of its decomposition products, namely the monoxide, Ag_2O, and a suboxide of silver.

Preparation of AgO from silver nitrate solution by controlled oxidation with alkaline hypochlorite at 75°—85°C has been reported by Dutta (1955).

Single crystals and powdered samples of Ag_7NO_{11}, erroneously described as Ag_2O_3, have also been studied by X-ray diffraction, and a face-centred cubic structure with a cube edge of 9.870 A.U. has been derived (Braekken 1935; Barbieri and Malaguti 1950).

Neiding and Kazarnovskii (1951) studied the properties of AgO, prepared by the deomposition of the peroxynitrate, Ag_7NO_{11}, with boiling water. The latter was obtained by the anodic oxidation of silver nitrate solution. They observed that dilute acids (H_2SO_4, HNO_3) gave no H_2O_2 by their action on AgO; concentrated nitric acid gave a dark brown solution, which on dilution with water and heating evolved oxygen and became colourless. The electrical conductivity of AgO, pressed under 12,000 kg/sq. cm at 20°C, was found to be 7×10^{-2} ohm^{-1} cm^{-1} ± 15 per cent., the temperature coefficient between $-40°$ and 20°C being positive. The substance thus behaved as an electronic semi-conductor. The specific heat of AgO, as determined by Jirsa (1949), is given by 0.0869 ± 0.0005.

Specimens of the oxide, AgO, prepared by different methods,—such as the oxidation of metallic silver with ozone or a mixture of ozone and oxygen, oxidation of Ag^+ with persulphate, the hydrolysis or thermal decomposition of Ag_7NO_{11},—showed the same powder patterns, and effectiveness as catalysts for the decomposition of ozone (Schwab and Hartman 1955).

Samples of higher oxides of silver were prepared by Graff and Stadelmaier (1958) by several chemical and electrochemical methods; viz. by the reaction between potassium persulphate and $AgNO_3$ solution, by anodic oxidation of $AgClO_4$ in aqueous perchloric acid or of AgF in aqueous hydrofluoric acid and of $AgNO_3$ in aqueous nitric acid, as well as of porous sintered silver in aqueous caustic potash. Two distinct higher oxides of silver were obtained as products. The one with bipositive silver, AgO, was found to form a black powder and possess a monoclinic structure with lattice constants: $a = 5.842$, $b = 3.480$, $c = 5.487$ A.U.; $\beta = 107° \ 27'$. The authors found no evidence for the existence of other crystalline forms of AgO. Another higher oxide, also of black colour, was found to be associated in some proportions with AgO and to show a positive valency of greater than two with a face-centred cubic lattice. This higher oxide suffered slow decomposition to AgO on keeping for months.

The peroxide obtained by the anodic oxidation of silver salts is quite stable at room temperature, but suffers decomposition at higher temperatures, even in alkaline solution (Dirkse and Wiers 1959).

The crystal structure of the oxide, AgO, has been investigated by Scatturin *et al.* (1958) in order to determine the type of coordination and the bond distances of Ag(II) by the powder method of X-ray analysis. It has been found that the compound is monoclinic in structure and resembles very closely the structure of CuO (tenorite) with a planar configuration of the oxygen atoms around the silver atom. The presence of two different Ag−O distances in the structure, viz. (1) 2.04 A.U. and (2) 2.35 A.U., which are commonly found in compounds of silver with formal valence of one and two respectively, has been discussed by the authors. Of the dsp^2 hybridization, which should characterize Ag(II), only the planarity of the silver-oxygen groups is maintained.

The magnetic susceptibility of AgO has been measured by various workers with a view to obtain information regarding the valency state of the silver atom in the compound. A bipositive silver ion, Ag^{2+}, having one unpaired electron in the 4d shell should behave magnetically like Cu^{2+} ion with one unpaired 3d electron and a paramagnetic moment of about 1.73 B.M. But the oxide, AgO, is practically diamagnetic (Klemm 1931; Sugden 1932). The compound has been found to remain diamagnetic at temperatures between −183° and +95°C; χ_g at room temperature $=0.155\times10^{-6}$ (Neiding and Kazarnovskii 1951). The observed diamagnetism has been attributed by these latter authors to the formation of metallic or covalent bonding between the silver atoms in the crystal lattice. In the light of McMillan's study (1960) on the structure of AgO by X-ray analysis the diamagnetism of the compound may be readily accounted for, as it may then be represented as a mixed oxide of the composition, $Ag_2O.Ag_2O_3$ with the tripositive silver being linked to four oxygen atoms in a planar configuration. Alternatively, the compound might be regarded as a peroxide of silver having the composition Ag_2O_2. But the balance of evidence, as discussed above, is against the formulation of the compound as a peroxide.

On the other hand, paramagnetism has been observed for the compound obtained by the action of ozone on strongly acidified (HNO_3) silver nitrate solution. It gave a moment value corresponding very closely to that expected for Ag^{2+} (Noyes, Pitzer and Dunn 1935). A moment of 1.76 B.M., which is in perfect agreement with the theoretical value for Ag^{2+}, has been reported for the peroxynitrate, Ag_7NO_{11}, by Neiding and Kazarnovskii (1951).

McMillan (1954, 1960) has closely investigated the structure of AgO by X-ray analysis and has obtained the same results as those reported by Graff and Stadelmaier (1958), as well as by Scatturin *et al.* (1958). The substance was found to form a monoclinic lattice belonging to the space group $C2/c - C_{2h}$ with the positions Ag(4d), O(4e). The choice of such a space group involves the assumption of four bivalent silver ions per unit cell. The results also indicate that silver ions are located in a face-centred cubic lattice, which gives the separation of neighbouring silver ions a value of 3.28 A.U. These observations agree equally well with the assumptions that all the four silver atoms are equivalent and occur as Ag(II), as well as that two of the silver atoms occur as Ag(III) and two as Ag(I) arranged in suitable planes with a somewhat lower symmetry space group $P2_1/c - C_{2h}$. As AgO has been found to be diamagnetic, while a true silver(II) oxide should show a paramagnetic moment corresponding to one unpaired electron, the formation of a metallic or a covalent Ag–Ag bonding has been postulated to account for this anomalous behaviour (Neiding and Kazarnovskii 1951). Such an explanation according to the author (McMillan 1960) is unsatisfactory since the metallic bonding should lead to much higher values of the conductivity, and the Ag(II)–Ag(II) covalent bonding between two bipositive kernels of small radius is not energetically feasible. He, therefore, assumes that in a unit cell of AgO, two of the silver atoms occur as Ag(III) and the other two as Ag(I). The tripositive silver ions are each coordinated with four oxygen, two of them being closer (dp hybridization) than the other two (sp hybridization). Of the four oxygen of the unit cell, two are the nearest neighbours of each Ag(I) ion, which suggests a linear sp coordination as is usual in covalent silver(I) compounds. The dark black colour of AgO has been attributed to the Ag–O bonding, the colour deepening with the increasing covalent character of the Ag–O bond (Helmholz and Levine 1942). The following distances between the neighbouring ions in AgO have been derived by the author (McMillan 1960).

Ag(III) – O $\cong$ Ag(I) – O $\cong$ 2.1 A.U.; this is comparable to the value found in Ag_2O for the distance Ag(I) – O = 2.06 A.U.
O – O $\cong$ 2.8 A.U. > 2.64 A.U. (ionic diameter of oxygen)
Ag(III) – Ag(III) = Ag(I) – Ag(I) = 3.28 A.U.
Ag(III) – Ag(I) = 3.39 A.U. Cf. Fig. 1.

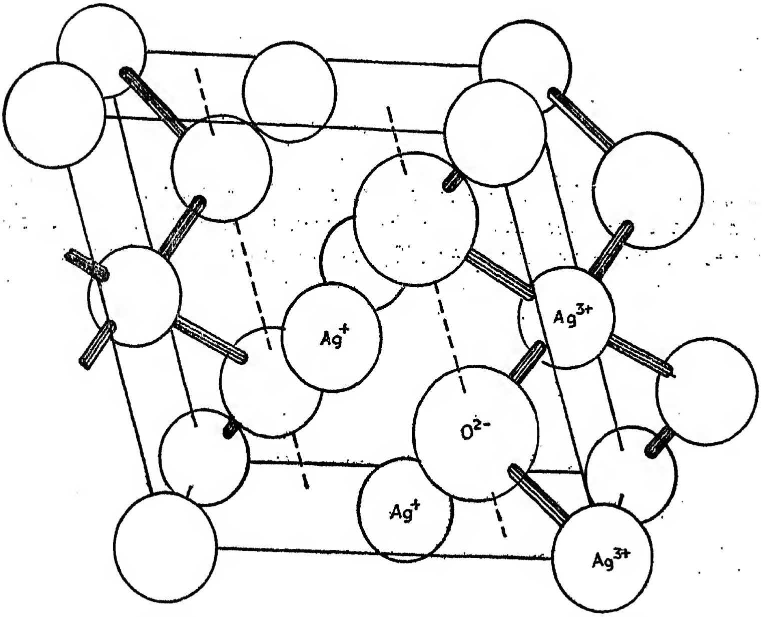


Fig. 1. Arrangement of atoms in AgO. (By courtesy, the author and Pergamon Press Ltd.)

It is claimed that most of the physical and chemical properties of AgO can be satisfactorily explained on this basis. This has been confirmed by the same author in his recent examination (private communication) of AgO in KOH by the method of paramagnetic resonance. Contrary to Dirkse and Wiers' (1959) finding he, therefore, concludes that there are no Ag^{2+} in alkaline solution; it breaks up into Ag^{+} and Ag^{3+} with possible formation of $Ag(OH)_2^-$ and $Ag(OH)_4^-$ respectively.

McMillan (private communication) has also studied the paramagnetic resonance spectrum of Ag^{2+} in frozen acid solutions (HNO_3, H_2SO_4) at 77°K, which can be interpreted as a doublet (interaction with silver nuclei) of strong g-anisotropy.

From all available evidences it appears now that in its combination with oxygen silver does not occur in the bipositive state, but either in the unipositive state as Ag_2O or in a mixed uni- and tripositive states as a molecular compound represented by the formula, $Ag_2O.Ag_2O_3$. The tripositive silver oxide, Ag_2O_3, has not been isolated in the free and pure state as yet.

An excellent review article by Dirkse (1959) on silver oxide electrodes and the oxides of silver has recently appeared in the Journal of Electrochemical Society to which a special reference might be made.

AgO has been found to serve as a powerful oxidimetric reagent in acid medium for analytical purposes. Methods for the volumetric estimation of vanadium, chromium, manganese and cerium have been described, using AgO as the oxidizing agent (Tanaka 1954; Lingane and Davis 1956). Colorimetric determination of vanadium has also been reported (Tanaka 1954).

(b) SILVER(II) FLUORIDE.

Silver(II) fluoride, AgF_2, has been prepared as a dark-brown or black solid by the direct combination of the elements at 150°—300°C and by the action of fluorine on silver(I) halides (Ebert *et al.* 1933; Ruff and Giese 1934). The compound has also been obtained in the form of a yellow solid by heating powdered silver in a current of fluorine at 250°C in a magnesium vessel (Jockush 1934). Rochow and Kukin (1952) used chlorine trifluoride in the preparation of silver(II) fluoride from AgCl.

Silver(II) fluoride reacts violently with water yielding oxygen and ozone with formation of Ag_2O and an oxidizing solution which possibly contains fluoric acid. Silver fluoride is a powerful oxidizing as well as a fluorinating agent. It can easily oxidize ethanol to acetaldehyde, manganous salts to permanganate, chromic salts to chromates, etc. It reacts with SO_2 and CO to form SO_2F_2 and COF_2, and converts CCl_4 to CF_4 (Ebert *et. al.* 1933; Jockush 1934).

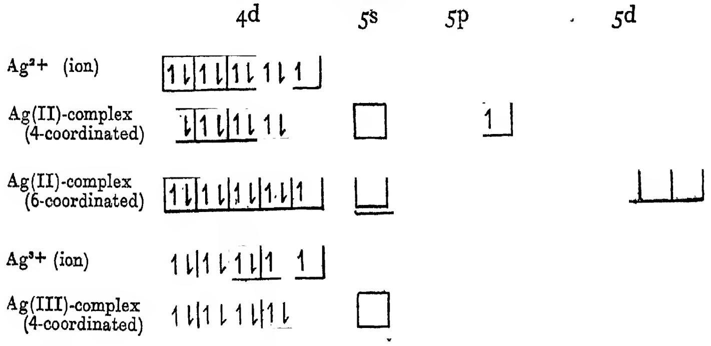
The heat of formation of AgF_2 by direct synthesis was found to be 84.5±1.2 kcal/mole, and its thermal stability is demonstrated by the fact that it melts at about 690°C with virtually no decomposition and that its decomposition pressure at 700°C is less than 0.1 atm. (Wartenberg 1939).

Silver(II) fluoride presents an interesting phenomenon in its magnetic behaviour. Gruner and Klemm (1937) obtained for AgF_2 a surprisingly low molar susceptibility of $+ 440 \times 10^{-6}$ at 20°C independent of the field. This is far below the theoretical value for one unpaired electron. But a sharp rise in the paramagnetic susceptibility occurs with the lowering of temperature when a weak ferromagnetism is attained at very low temperatures with a well-defined Curie point at -110°C. The mass susceptibility at this point is given by the value 270×10^{-6}. It is, therefore, assumed that the compound shows antiferromagnetism with metallic (antiparallel spins) Ag–Ag bonds at high temperatures, but assumes a weak ferromagnetic character with parallel spins at low temperatures.

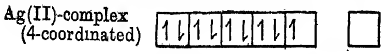
II. COMPLEX COMPOUNDS.

The higher oxidation states of silver are usually stabilized by complex formation, particularly in combination with ligands offering the possibility of formation of dative π-bonds (Orgel 1956).

Many well-defined and crystalline complex compounds of both bi- and tripositive silver have been described in the literature. With few exceptions in the case of silver(II) complexes they all form 4-covalent penetration or inner level square planar complexes with dsp^2 hybrid bonds (Rây 1946). All the bipositive silver complexes show a paramagnetic moment of c. 1.73 B.M. while the tripositive complexes are diamagnetic, in conformity with their electronic configurations as represented below.


4d
5s
5p
5d
Ag^{2+} (ion)
Ag(II)-complex (4-coordinated)
Ag(II)-complex (6-coordinated)
Ag^{3+} (ion)
Ag(III)-complex (4-coordinated)

Associated or outer level complexes with sp^3 or sp^2d bonds.



Squares covered by the brackets indicate orbitals available for bond formation.

But the properties of the bipositive silver complexes with moment values of c. 1.73 B.M. with practically little contribution from the orbital moment justify their representation as inner level complexes with dsp^2 hybrid bonds. With the unpaired d-electron promoted to the outermost level, exposed to the influence of the field of the neighbouring atoms and ions, there is every likelihood of its orbital moment being completely quenched (Rây and Sen 1948).

It is also worthy of note that the number of 6-coordinated or octahedral complexes of bipositive silver is rather limited. Even the tripositive silver with its higher charge has not yet been found to give any 6-coordinated complex. This might be attributed to the comparatively high electronegativity of silver which in consequence derives an adequate share of electrons from a relatively smaller number of ligands to satisfy Pauling's "postulate of neutrality" (Pauling 1945). In this respect tripositive silver resembles closely the tripositive gold.

(a) SILVER(II) COMPLEXES.

The bipositive state of silver has been found to be stabilized in complexes with a number of organic ligands of the type of heterocyclic nitrogen bases. The oxidation potential of Ag(I) to Ag(II) is rather high, being 1.914 volts (Noyes and Kossiakoff 1935) in acid (HNO_3) solution and 1.41 volts (Luther and Pokorny 1908) in alkaline solution ; but these values are considerably lowered by coordination. This has made possible the preparation of a number of more or less stable bipositive silver complexes with suitable ligands, particularly of the chelating type.

The orange-coloured prismatic crystals of $[Ag^{II}(py)_4]S_2O_8$ (where py = pyridine), isomorphous with $[Cu^{II}(py)_4]S_2O_8$, were obtained by Barbieri (1912) by oxidizing an aqueous solution of silver nitrate in pyridine with potassium persulphate. The complex persulphate is unaffected by light. The corresponding nitrate, $[Ag^{II}(py)_4](NO_3)_2$, was prepared electrolytically in the form of orange-red needles from aqueous pyridine solution in a divided cell. The compound was isolated in small yield from the anode liquor which was composed of 8-10 per cent. silver nitrate and 40 per cent. pyridine, the cathode solution being 10-15 per cent. sulphuric acid placed in a porous cup. A current of 0.2-0.6 amp. at 5-6 volts between Pt-electrodes was employed for the preparation.

Mixed crystals of silver(II) and cadmium(II) pyridine persulphate, $[Ag_x^{II}Cd_y^{II}(py)_4]S_2O_8$, have been obtained by oxidizing a mixture of silver(I) and cadmium(II) salts with $K_2S_2O_8$ in presence of pyridine. This serves as an evidence that silver occurs in the bipositive state in the silver pyridine complex prepared by oxidation (Barbieri 1931).

Magnetic properties of mixed crystals of silver(II) and copper(II) pyridine complexes, $[Ag_x^{II}Cu_{(1-x)}^{II}(py)_4]S_2O_8$, have been studied by Capatos and Perakis (1936). The Curie point and the Curie constant were both found to vary with concentration (x). The curves show at first a linear drop in the constant and a rise in the point as x changes from either 0 or 1, followed in both cases by an abrupt reversal in direction to a maximum for the constant and a minimum for the point at $x = 0.5$ (Fig. 2).

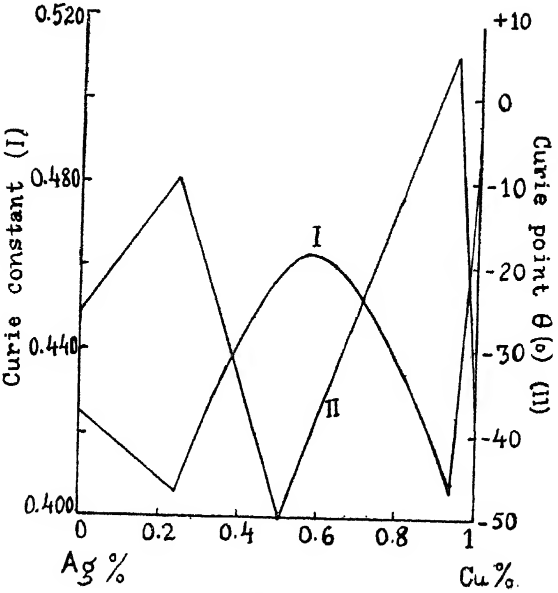


Fig. 2

Perakis and Capatos (1938, 1939) have made a thermomagnetic study of the complexes $[Ag_x^{II}Cd_y^{II}(py)_4]S_2O_8$ and $[Cu_x^{II}Cd_y^{II}(py)_4]S_2O_8$ in the liquid air to room temperature interval for a wide range of concentrations of silver and copper. In mixtures very weak in copper and silver the curves giving the variation of the magnetic moment and Curie point as functions of the concentration have approximately the same form and direction in the two systems. In mixtures rich in copper and silver the moments vary but little with concentration. In the more dilute solutions at a certain concentration the moment increases suddenly and approaches, at least for silver, the theoretical moment of the Ag^{3+} ion (14 Weiss magnetons). Cf. Fig. 3. If it be assumed as an explanation that silver(II) suffers disproportionation into silver(III) and silver(I) on magnetic dilution, then there would occur some reduction in the net moment value of the system, assuming the complex to be ionic. The authors' explanation is therefore untenable. This

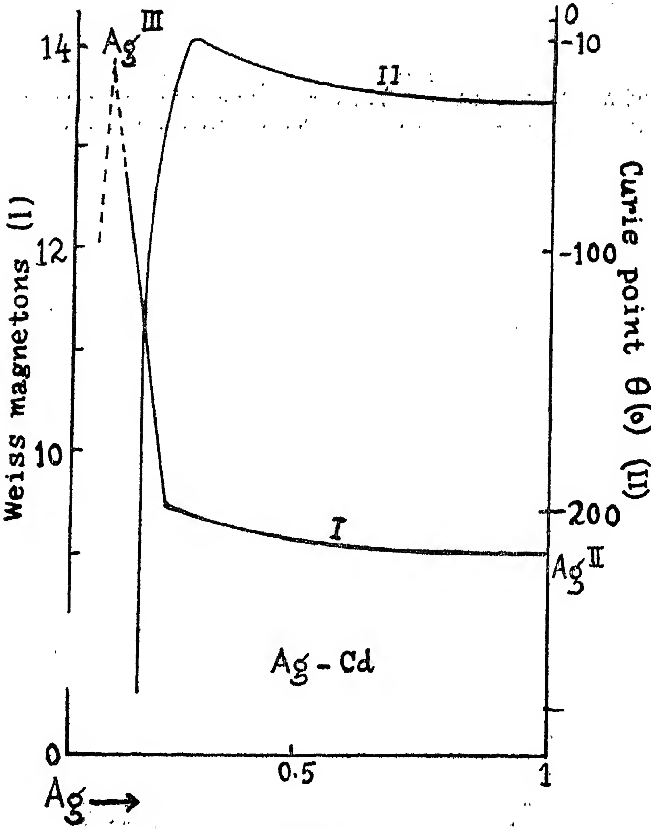
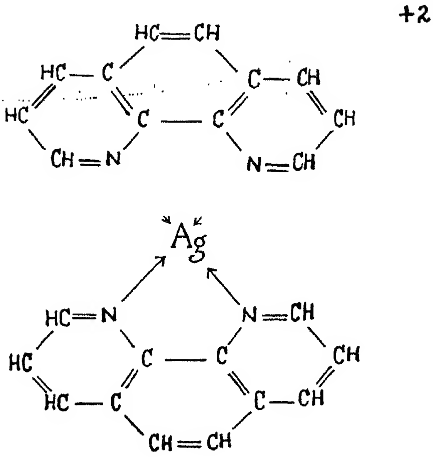


Fig. 3

strange observation consequently arouses some suspicion, regarding the purity of the samples under study, or of their adventitious contamination with traces of paramagnetic or ferromagnetic impurities.

Hieber and Mühlbauer (1928) have described the preparation of reddish brown [Ag^{II}(*o*-phen)$_2$] S_2O_8 (*o*-phen = *o*-phenanthroline) in quantitive yield from a solution of silver nitrate by oxidation with ammonium persulphate in presence of an excess of *o*-phenanthroline. From a solution of the complex persulphate in 64 per cent. HNO_3 the corresponding perchlorate, chlorate, nitrate and hydrogen-sulphate have been obtained by treatment with the appropriate alkali salts. The phenanthroline complexes are quite stable and are isomorphous with the corresponding copper(II) and cadmium salts. The complex silver(II) phenanthroline ion is represented by the configuration I.

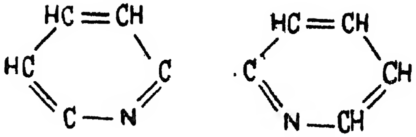


I

Using αα-dipyridyl (vide II) as the chelating ligand Morgan and Burstall (1930) prepared a number of complex silver(II) salts in the form of red crystals from hot aqueous alcoholic solution of silver nitrate by oxidation with potassium persulphate. Two types of compounds were isolated by the authors with two and three molecular proportions of αα-dipyridyl showing coordination numbers of 4 and 6 respectively:

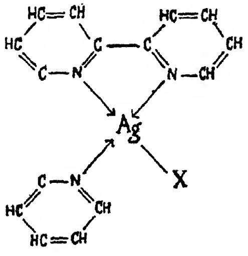
$[Ag^{II}(dipy)_2]S_2O_8$ or $(HSO_4)_2$ and $[Ag^{II}(dipy)_3]X_2$;
where $X = NO_3$, ClO_3, or ClO_4.

A binuclear compound of the composition, $[Ag_2^{II}(dipy)_5](S_2O_8)_2$, has also been described. In a similar manner tripyridyl complexes of bipositive silver of composition $[Ag^{I}{}_{1}(trpy)X]X$ and $[Ag^{II}(trpy)S_2O_8]$ have been prepared by the same authors (1937), and are represented by square planar structure (III *a* and *b*).



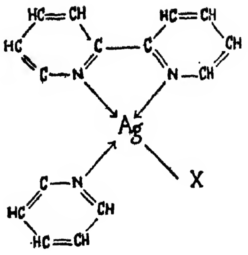
II

Nitrate, perchlorate and bisulphate of silver(II) dipyridyl complex, $[Ag^{II}(dipy)_2]X_2$ (where $X = NO_3$, ClO_4 or HSO_4), have also been prepared by electrolytic oxidation in a divided cell (Barbieri 1932).



$[X = ClO_3^-, ClO_4^-, NO_3^-]$

IIIa



$X = S_2O_8^{=}$

IIIb

In the preparation of silver(II) complexes of αα-dipyridyl and o-phenanthroline, potassium persulphate can be replaced by the common oxidizing agents like PbO_2, BaO_2, CeO_2, etc., none of which are effective in oxidizing Ag to Ag^{2+} in the absence of any complexing agent (Malaguti 1950).

All the silver(II) complexes are strong oxidizing agents. In their molecules the silver atom is coordinated with 4 or 6 (in *tris*-dipyridyl complexes) nitrogen atoms provided by the ligand molecules, forming a square planar or octahedral structure as the case may be.

The preparation of a deep green silver complex of oxine, having the composition, $[Ag\ (oxine)_2]$, was reported by Nakatsuka (1936), in which the silver atom was believed to occur in the bipositive state. This was precipitated from a hot solution of silver(I) acetate by the addition of 8-hydroxyquinoline (oxine) without the use of any oxidizing agent. But Block, Bailar and Peace (1951) have shown that the compound, which can be obtained in two coloured forms, yellow and green, gives no evidence for any higher oxidation state of silver present in it. Moreover, the green variety, which was examined magnetically, was found to be diamagnetic like all compounds of univalent silver.

Malaguti and Labianca (1954) have made use of ozone as an oxidizing agent for the preparation of silver(II) complexes. In the case of dipyridyl salts, $[Ag^{II}(dipy)_2]X_2$ ($X = NO_3$, ClO_3 or ClO_4), an almost quantitative yield has been reported. The following procedure was adopted for their preparation. The dipyridyl silver(I) nitrate, $[Ag^I\ (dipy)_2]NO_3$, which separates as a precipitate on mixing a solution of silver nitrate with dipyridyl, was dissolved in the particular acid containing the anion of the complex salt under preparation. The solution was then saturated with the sodium salt of the anion involved and treated with ozone until the precipitation of the complex salt was complete.

$$2[Ag^{I}(dipy)_2]^+ + 2H^+ + O_3 \rightarrow 2[Ag^{II}(dipy)_2]^{2+} + H_2O + O_2$$

Ozone does not oxidize dipyridyl. The procedure is applicable to the preparation of silver(II) complexes of phenanthroline and other organic bases.

The standard oxidation-reduction potential of silver(II) dipyridyl complexes has been determined by Scrocco, Marmani and Mirone (1950). The value obtained is given by 1.453 volts. This is much smaller than those found for the system Ag^+-Ag^{2+} in $HClO_4$ and HNO_3 solutions, viz. 2.0 and 1.929 volts respectively. The temperature coefficient also of the redox potential of the system,
$[Ag^I(dipy)_2]^+ — [Ag^{II}(dipy)_2]^{2+}$, in nitric acid solution has been determined by Scrocco and Marmani (1954) and the value found is 0.0012 volt/degree.

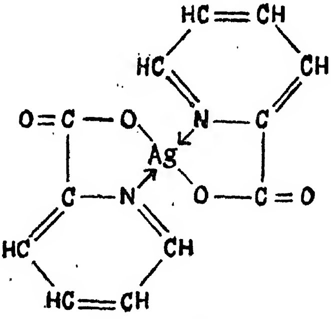
Solutions of $[Ag^{II}(py)_4]^{2+}$, $[Ag^{II}(o\text{-phen})_2]^{2+}$ and of $[Ag(oxine)_2]$(?) are all coloured red or brown with strong absorption at 3500–4000 A.U. (Sone 1949).

Bruno and Santoro (1956) studied the exchange reaction of the radioactive Ag^{110}-ion between silver nitrate and complex silver(II) compounds of αα-dipyridyl and o-phenanthroline. The silver(II) complex was separated by precipitation with $NaClO_4$ solution and Ag^+ by HCl. It was found that the total exchange occurred after 2 minutes. This seems to suggest that Ag^{2+} resulting from the dissociation of the complex suffers a partial disproportionation leading to the equilibrium:

$$2Ag^{2+} \rightleftharpoons Ag^+ + Ag^{3+}.$$

In these silver(II) complexes, which are usually 4-covalent, the bonds are assumed on the basis of Pauling's theory (1945) to be of the hybrid dsp^2 type giving rise to a square planar structure with a spare electron in the p_z orbital. The smaller difference in the free energy between silver(I) and silver(II) complexes of αα-dipyridyl and o-phenanthroline than the corresponding difference in their ionic states Ag^+ and Ag^{2+} has been attributed by Scrocco and Ragazzini (1954) to the formation of covalent bonds with donor groups plus the stabilizing effect of the unpaired p_z electron resonating with similar electrons of the aromatic nuclei. With a view to confirm this assumption the authors made the measurement of redox potentials of silver(I) and silver(II) complexes of both αα-dipyridyl and o-phenanthroline. A decrease of 65 mv in the redox potential was observed in the case of phenanthroline complexes, since the number of electrons with which the silver(II)-p_z-electron can interact is increased by 4 in the case of phenanthroline complex over that of the dipyridyl complex.

A very stable chelate complex of bipositive silver of the inner metallic type with picolinic acid (pyridine-2-carboxylic acid), $[Ag^{II}(C_6H_4NO_2)_2]$, was described by Barbieri (1933). It was obtained in the form of sparingly soluble, orange-red needles by the oxidation of silver nitrate solution with potassium persulphate in the presence of an excess of picolinic acid, rendered alkaline with sodium carbonate. Electrolytic oxidation with platinum electrodes was also found equally effective for its preparation. In the presence of a copper salt mixed crystals containing both silver and copper were found to separate. The complex is decomposed by HCl with evolution of Cl_2 and precipitation of AgCl. Ammonia and hydrogen peroxide are oxidized by it with evolution of N_2 and O_2 respectively. Cox *et al.* (1936) have shown by X-ray analysis that the compound has a square planar configuration IV and is isomorphous with coplanar copper complex of the same ligand. It shows moreover the high birefringence expected for a parallel arrangement of coplanar molecules.

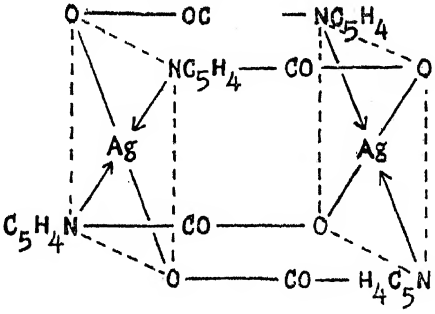


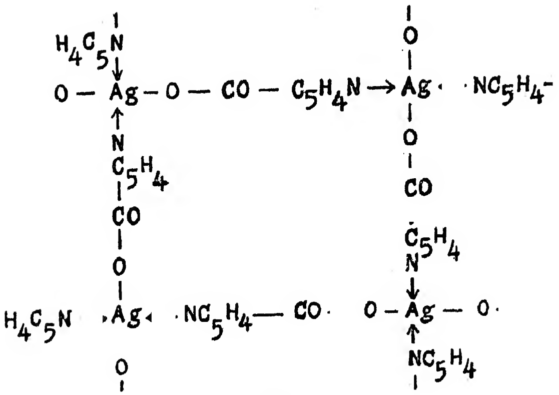
IV

Silver(II) picolinate is, therefore, a quadricovalent complex with dsp^2 hybrid bonds.

Banerjee and Rây (1956) have described the silver(II) complexes of nicotinic acid (pyridine-3-carboxylic acid) and of isonicotinic acid (pyridine-4-carboxylic acid). These were obtained in the form of insoluble cinnamon-red crystals by treating a cold aqueous solution of the chelating ligand concerned with silver nitrate and potassium persulphate solution. The complexes are more or less readily decomposed by dilute mineral acids and alkalies. They show a paramagnetic moment of c. 1.73 B.M., corresponding to the presence of one unpaired electron expected for a simple or complex bipositive silver compound. The silver(II) isonicotinate was found to be isomorphous with the corresponding copper(II) compound from an X-ray study of their powdered crystals. An indication of similar isomorphism for the nicotinate complexes of bipositive silver and copper has also been reported (Chackraburtty and Banerjee 1955) in view of the general resemblance of their X-ray patterns. From a consideration of their properties they are best represented as inner metallic quadricovalent silver(II) complexes with coplanar dsp^2 hybrid bonds. But because of the possibility of steric hindrance to the bridging of meta- and parapositions of the aromatic ligands with formation of six- and seven-membered rings, the authors represent their structure as made up of either dimeric molecules as in V, or of polymeric molecules as in VI with the formation of an unending two-dimensional sheets and layers. An X-ray analysis of their structures is needed to arrive at a final conclusion on the matter.

Silver(II) complexes of the five out of six different pyridine dicarboxylic acids, viz., quinolinic (2:3), cinchomeronic (3:4), isocinchomeronic (2:5), lutidinic (2:4) and dipicolinic (2:6) acids have also been described by Banerjee and Rây (1957). These were prepared in the same manner as the silver(II) complexes of pyridine monocarboxylic acids and form more or less sparingly soluble red to dark-red crystals. The silver(II) dipicolinate was isolated, however, in two differently coloured modifications, dark-red (with $2H_2O$) and green (with $4H_2O$), differing in their water of hydration. The composition of these silver(II) complexes of pyridine dicarboxylic acids is represented by the general formula $[Ag^{II}(BH)_2]$, where BH_2 = one molecule of the acid concerned. Obviously one of the two —COOH groups





VI

of each ligand molecule remains free and inactive. All these complexes are more or less readily decomposed by dilute mineral acids and alkalies. They all showed, as expected, a magnetic moment of 1.73 B.M. approx. The X-ray diffraction patterns with data for the silver(II) quinolinate and for the two (dark-red and green) modifications of silver(II) dipicolinate have also been furnished by the authors. The preparation of a silver(II) quinolinate with $1H_2O$, $[Ag^{II}(BH)_2].H_2O$, which thus differs from that described by Banerjee and Rây in its water of hydration, was reported much earlier by Burada (1935). This was, however, prepared by oxidiing *bis*-quinoline silver(I) nitrate, $[Ag^{I}(C_9H_7N)_2]NO_3$, with ammonium persulphate in aqueous solution.

The structure of silver(II) complex of cinchomeronic acid is presumably related to that of nicotinic and of isonicotinic acid, being either dimeric, or polymeric with the formation of unending two-dimensional sheets or layers. Silver(II) complexes of all the other pyridine dicarboxylic acids are probably represented by a monomeric structure like that of silver(II) picolinate (Banerjee and Rây 1957).

Banerjee and Rây (1957) have further reported the preparation of silver(II) complexes of some of of the pyridine tricarboxylic acids, namely, pyridine-2:3:6-, -2:4:5- and -2:4:6-carboxylic acids by oxidation of silver nitrate in cold aqueous solution with persulphate in presence of the acid concerned. The silver(II) complex of 2:3:6-tricarboxylic acid of pyridine, however, forms a very unstable green compound, decomposing even at 5°C in vacuum. Pyridine-2:4:6-tricarboxylic acid (collidinic acid) like dipicolinic acid gave two differently coloured products, chocolate and black. The former was found to crystallize with one molecule of water and the latter to separate in the anhydrous state. The silver(II) complex of pyridine-2:4:5-tricarboxylic acid forms beautiful orange-coloured microcrystals. The properties of these compounds are more or less similar to those of the silver(II) complexes of mono- and dicarboxylic acids of pyridine. They show a magnetic moment value of about 1.73 – 1.82 B.M. Their compositions can be represented by the general formula, $[Ag^{II}(BH_2)_2]$, where BH_3 = one molecule of the pyridine tricarboxylic acid concerned. Two of the three —COOH groups in each molecule of the ligand remain free. The X-ray powder photographs with data for the two forms of silver(II) collidinate, chocolate and black, have also been presented by the authors.

The stability of the silver(II) complexes of pyridine mono-, di- and tricarboxylic acids has been found to vary in the order complex (monoacid) > complex (diacid) > complex (triacid). Within each group again the stability varies depending on the relative positions of the functional groups and of the inactive —COOH groups where present. The steric effect that hinders the formation of favourable planar configuration around the central silver atom reduces the stability of the complex.

All the quadricovalent silver(II) complexes, that have been examined magnetically, show a paramagnetic moment value of 1.73 B.M. approx. in perfect agreement with that expected theoretically for one unpaired electron (Klemm 1931; Morgan and Sugden 1931; Sugden 1932; Capatos and Perakis 1936; Banerjee and Rây 1956, 1957). A few silver(II) dipyridyl complexes described by Morgan and Burstall (1930), which show a coordination number of six, give on the other hand a somewhat higher moment value of 2.03 – 2.16 B.M. In these latter, therefore, the orbital moment is not completely quenched. For, a sexicovalent silver(II) complex, like the corresponding copper(II) complex, can at best be an associated or outer level complex with sp^3d^2 hybrid bonds (Rây and Sen 1948).

Paramagnetic resonance studies on the *bis-o*-phenanthroline silver(II) persulphate, $[Ag^{II}(o\text{-phen})_2]S_2O_8$, indicate that the electron hole in the 4d subshell is not localized on the silver(II) ion, but migrates to the surrounding atoms (Bowers 1953). This seems to suggest the formation of π-bonding.

The silver(II) dipyridyl complex, $[Ag^{II}(dipy)_2]^{2+}$ has been found to serve as an oxidimetric titrant for the determination of oxalic acid, nitrous acid and quadrivalent vanadium (Barbieri and Labianca 1954).

(*b*) SILVER(III) COMPLEXES.

There are evidences for the occurrence of Ag^{3+} in the form of simple salts in solution, though it has not been possible to isolate them in a pure solid state.

Barbieri (1931) studied the product formed by dissolving AgO in conc. HNO_3. The ratio of Ag:O (active) in the solution was determined by oxidimetric titration with various reagents. A ratio of 1:1.5-1.6 was obtained in all cases indicating the existence of Ag^{3+} in solution. The author, therefore, suggested that AgO dissolves in nitric acid with disproportionation into silver(I) and silver(III) nitrates:

$$2AgO + 4HNO_3 = Ag(NO_3)_3 + AgNO_3 + 2H_2O.$$

From a study of the kinetics of the isotopic exchange reaction between Ag(I) and Ag(II) in perchloric acid solution Gordon and Wahl (1958) have proposed that the exchange occurs via the reaction,

$$2Ag^{2+} \rightleftharpoons Ag^{+} + Ag^{3+} \quad \text{(cf. Bruno and Santoro 1956).}$$

Ag^{3+} has, however, been remarkably stabilized by complex formation with some suitable ligands capable of yielding dative π-bonds and/or polycyclic rings with the metal atom.

The electrolytic oxidation of telluric acid at a silver anode is said to yield a compound having the composition represented by the formula, $5Ag_2O_3.Ag_2O.9TeO_3$ (Brauner and Kuzma 1907). No analytical results have, however, been furnished by the authors. Apparently it is a basic salt containing some univalent silver.

Malaprade (1940) reports the isolation of a crystalline compound from the brown solution resulting from the oxidation of Ag_2O with a boiling concentrated solution of KOH and KIO_4. The product after recrystallization from aqueous KOH gave on analysis the atomic ratio of K:Ag:I = 6:1:2. On treating the brown solution with NaOH a salt was precipitated in which the ratio Na:K:Ag:I was found to be equal to 4.5:1.5:1:2. The determination of available oxygen demonstrated the tripositive character of the silver atom in the compounds. With dilute acids the substances gave ozonized oxygen. The author has not given any definite composition for the products. They may obviously be represented by the formula, $M_6H\,[Ag^{III}(IO_6)_2]$; where M = K or K + Na. A compound of this composition has subsequently been described by Malatesta (1941).

The preparation of a number of strongly coloured crystalline periodates of tripositive silver of the general formula, $M_7\,[Ag^{III}\,(IO_6)_2].xH_2O$, has been described by Malatesta (1941). The compounds are all diamagnetic and should for this reason, on the basis of valence bond theory, be regarded as quadricovalent complexes having square planar configuration with dsp^2 hybrid bonds. In these the tripositive silver atom is covalently bound with four oxygen atoms, two from each periodate (IO_6) group (cf. Rây and Sarma 1948). A tripositive silver atom, being isoelectronic with bipositive palladium, is likely to show a coordination number of four (vide Rây and Chakravarty 1944).

Oxidation of a mixture of Ag_2SO_4, KIO_4 and KOH with potassium persulphate in aqueous solution at the boiling temperature has led to the preparation of $K_6H\,[Ag^{III}(IO_6)_2].10H_2O$ in the form of orange crystals with a molar susceptibility (χ_M) of -40.5×10^{-6}. By rapid evaporation of the reaction mixture a compound of the composition, $K_7[Ag^{III}\,(IO_6)_2].KOH.8H_2O$, has been obtained. Treatment of the former compound with dilute sodium carbonate solution yields the orange-yellow compound, $KNa_5H[Ag^{III}\,(IO_6)_2]$ $.16H_2O$, with $\chi_M = -31.6 \times 10^{-6}$. This on treatment with dilute caustic soda solution and then with alcohol produces $KNa_6[Ag^{III}(IO_6)_2]\,.NaOH.H_2O$ of a dirty yellow colour.

In a similar manner the same author (Malatesta 1941) has prepared some complex tellurates of tripositive silver of the general formula, $M^I_9[Ag^{III}\,(TeO_6)_2].nH_2O$. Oxidation with potassium persulphate of a mixture of Ag_2SO_4, TeO_2 and NaOH in water at the boiling temperature yielded the pale yellow crystals of the compounds,

$Na_6H_3\,[Ag^{III}(TeO_6)_2].18H_2O$ with $\chi_M = 22 \times 10^{-6}$, and $Na_7H_2\,[Ag^{III}(TeO_6)_2]$ $.14H_2O$. Like the corresponding periodates they should also be regarded as quadricovalent silver(III) complexes having square planar configuration with dsp^2 hybrid bonds.

Malaprade and Coulombeau (1954) have found that the complex silver(III) periodate oxidized oxalic acid to CO_2. During the reaction, while Ag^{3+} is reduced to Ag^+, much of the periodic acid is simultaneously reduced to iodic acid. But as the cold dilute periodic acid has no action on oxalic acid, the reduction of periodic acid in the above reaction may be regarded as an instance of *induced reaction,* comparable to the reduction of mercuric chloride to mercurous chloride in a mixture of mercuric chloride and oxalic acid when the latter is oxidized with potassium permanganate in solution. Ag^{3+} behaves here in an analogous manner to permanganate, and periodic acid to mercuric chloride.

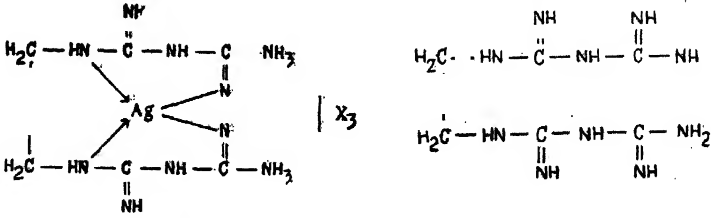
The preparation of a complex fluoride of tripositive silver, $KAgF_4$, has been reported by Klemm (1954). This is formed by the action of fluorine upon a mixture of AgF and KF. The substance was found to be diamagnetic.

Nakatsuka and Miwa (1952) have reported the preparation of a silver(III) complex with oxine by the action of silver(II) and silver(III) oxides on oxine in cold pyridine solution. It forms a yellowish brown, unstable product insoluble in water and many organic solvents, but highly soluble in pyridine. It oxidizes the halogen acids and decomposes in other acids.

Rây and Chakravarty (1944) have described a remarkably stable 4-covalent cationic complex of tripositive silver with ethylenedibiguanide. The complex base, $[Ag^{III}C_2H_4(C_2H_6N_5)_2](OH)_3.3H_2O$, is violet-red, while the salts, sulphate (with $7H_2O$), nitrate, and perchlorate (with $1.5H_2O$), form beautiful deep red needle-shaped crystals. The ethylenedibiguanide functions as a quadridentate chelating ligand and forms an inner metallic complex with the tripositive silver atom. The dibiguanide molecule behaves at the same time as a dibasic acid with two replaceable hydrogen atoms in two of its imino (= NH) groups, as well as a diamine base with its two amino (– NH_2) groups at the two ends. The complex base and its salts are all diamagnetic and are quite stable in the solid state. The nitrate can be recrystallized from hot dilute (2*N*) nitric acid without any change. As the electronic configuration of Ag^{3+} is closely analogous to that of Pd^{2+} and Ni^{2+}, the structure of the silver(III) ethylenedibiguanide compounds should, according to the authors, be represented by a square planar configuration with dsp^2 hybrid bonds (VII).

The complex silver(III) ethylenedibiguanide sulphate was prepared by persulphate oxidation of a mixture of Ag_2SO_4 and ethylenedibiguanide sulphate, $C_2H_4(C_2H_6N_5)_2.2H_2SO_4$ in cold aqueous solution. The substance is moderately soluble in water and loses its water of hydration ($7H_2O$) at 80°C. $\chi_g = -0.394 \times 10^{-6}$. The complex base was obtained from the sulphate by teratment with cold NaOH solution. It is sparingly soluble in cold water and reacts strongly alkaline to litmus. χ_g (base) = -0.39×10^{-6}.

The complex nitrate and the perchlorate were prepared from the base by treatment with cold dilute (1*N*) nitric acid and 60% perchloric acid respectively. The complex nitrate is moderately and the perchlorate is highly soluble in water. χ_g (nitrate) = -0.402×10^{-6}. The molecular conductivity of the nitrate, 518 ohm^{-1} at 20°C, corresponds to that of a tripositive complex ion (Rây and Chakrabarty 1944). A microphotograph of the crystals of the complex nitrate is shown in Fig. 4*a*.



VII.

Attempts to prepare similar complexes of tripositive silver with the simple biguanide, $C_2H_7N_5$, ended in failure, as the ligand itself was oxidized by the persulphate under the conditions employed for the preparation of the silver(III) ethylenedibiguanide complex. Investigations of Noyes *et al.* (1935, 1937), as well as of Luther and Pokorny (1908), have shown that the oxidation potential of Ag(I)–Ag(II) increases with the p_H value of the solution. In alkaline solutions it has been found to be much lower than in acid solutions. This also holds good for the oxidation to Ag(III) state. It might, therefore, be expected that by a proper adjustment of the p_H value of the solution Ag(I) may be oxidized to a higher positive state by persulphate oxidation, leading to a complex formation with the simple biguanide without the ligand itself being oxidized at the same time. This has actually been realized recently by one of us. Sen (1960) has just succeeded in preparing the silver(III) biguanide complex of the composition, $[\mathrm{Ag}^{\mathrm{III}}(C_2H_7N_5)_2](OH)SO_4.7H_2O$, in the form of sparingly soluble, brown silky crystals by oxidizing with potassium persulphate in cold aqueous solution a mixture of biguanide sulphate and silver(I) nitrate at a p_H 6.5–7.0. The substance was found to be diamagnetic with $\chi_g = -0.689\times10^{-6}$. Fig. 4*b* shows a microphotograph of its crystals. The complex hydroxide-sulphate was converted to the orange-yellow nitrate sulphate, $[\mathrm{Ag}^{\mathrm{III}}(C_2H_7N_5)_2](NO_3)SO_4.6H_2O$, by treatment with nitric acid (1*N*). From these the free complex base, as well as its nitrate and sulphate, have been obtained in the pure state. The complex is represented by a structure similar to that for silver(III) ethylenedibiguanide, preferably in a trans form VIII. Similar complexes of tripositive silver with some alkylbiguanides have also been obtained in the form of orange-coloured crystals.

Fig. 4a. Ag(III) Ethylenedibiguanide nitrate crystals.

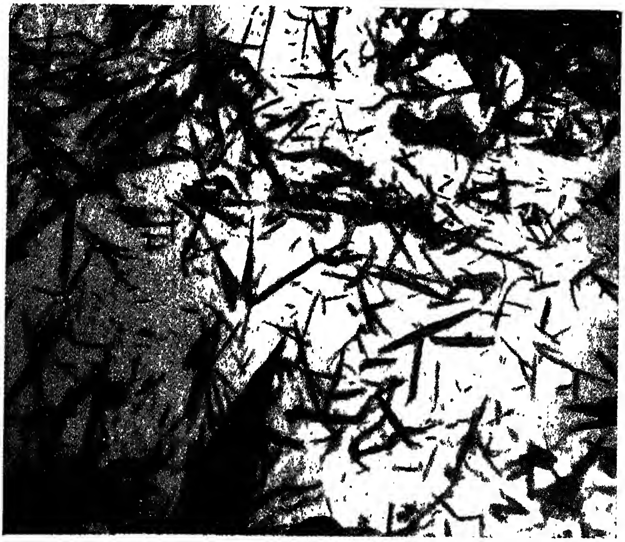
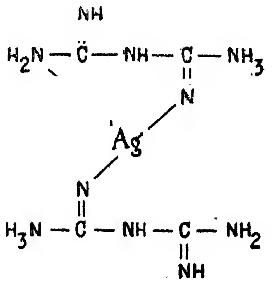
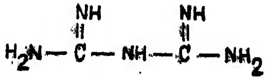


Fig. 4b. Ag(III) Biguanide hydroxide-sulphate crystals.

Curiously enough, with biguanide as a complexing ligand no bipositive silver complex has yet been obtained. An investigation with this end in view is, however, awaited with interest.

A solution of the complex silver(III) ethylenedibiguanide nitrate or sulphate has been found by the writers of the present review to show a wide band of absorbance maximum extending from 300–370 mμ with a molar extinction coefficient of 2325 (nitrate) and 2422 (sulphate) at 32°C.





VIII

Silver(II) complexes of pyridine and *o*-phenanthroline show, according to Sone (1949), a similar absorption band at 350–400 mμ. All these silver(II) and silver(III) complexes possess the same atomic configuration with the central silver atom being covalently linked to the four surrounding nitrogen atoms of the ligands in a square planar structure. The shifting of the absorption band towards the ultraviolet in the case of the silver(III) complex seems to suggest an increase in the strength of the Ag–N bond and hence an increased stability of the silver(III) complexes. This is not unexpected in view of the increased charge on the silver atom and is, in fact, supported by the general properties of the silver(II) and silver(III) complexes, as well as by the very high value of the instability constant of silver(III) ethylenedibiguanide nitrate in solution.

The stability of silver(III) ethylenedibiguanide nitrate in 2*N* KNO_3 solution has been determined by Sen, Ghosh and Rây (1950) from the equilibrium constant of the reaction between the complex salt and the hydrogen ion (HNO_3), using the acid dissociation constants of the ethylenedibiguanide base. The equilibrium constant was derived from the p_H and Ag^{3+} concentration of the equilibrated solution. The Ag^{3+} concentration was derived from a measurement of the redox potential of the equilibrated solution in the presence of Ag^+ ion. On the assumption of a single stage dissociation of the complex ion the value of its instability constant for the reaction ;

$$[Ag^{III}C_2H_4(C_2H_6N_5)_2]^{3+} \rightleftharpoons Ag^{3+} + C_2H_4(C_2H_6N_5)_2,$$

was found to be given by pK = 52.16 at 32°C. The value was also corrected for the decomposition of Ag^{3+} ion in solution according to the equation, $Ag^{3+} + H_2O \rightleftharpoons Ag^{+} + 2H^{+} + \frac{1}{2}O_2$.

The rate of decomposition of silver(III) ethylenedibiguanide nitrate at different p_H and temperatures (25°, 35° and 45°C) has been studied by Sen and Rây (1953). The reaction rate is p_H dependent, but the reaction proceeds in a rather complicated manner. The curves in Figs. 5 and 6 show the rate of decomposition of the complex nitrate in water and acid (HNO_3) solutions at 25° and 45°C. It is apparent from the slope of the curves that

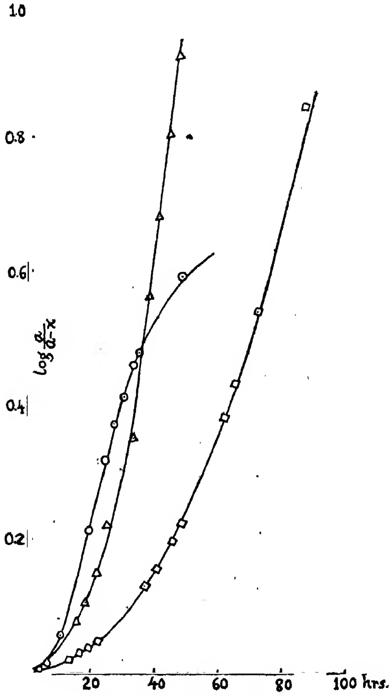


Fig. 5. temp. = 25°C.

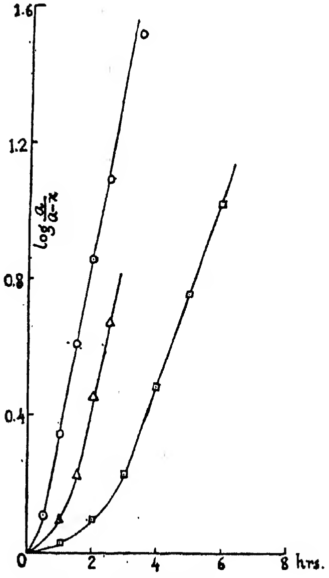


Fig. 6. temp. = 45°C.

—o—o— water solution.

—Δ—Δ— 0·025 *M* HNO_3 solution

—□—□— 0·05 *M* HNO_3 solution

a = initial concentration of the complex

$(a-x)$ = concentration of the total tripositive silver after a time t.

the decomposition is somewhat retarded in acid solutions. It has been suggested that in aqueous solution the decomposition occurs mainly through some intermediate stage with the formation of bipositive silver and hydrogen peroxide, while the direct decomposition of Ag^{3+} to Ag^+ predominates in acid solutions. The mechanism of decomposition has been represented by the following equations:

In acid solutions: $Ag^{3+} + H_2O \rightleftharpoons Ag^+ + 2H^+ + \frac{1}{2}O_2$;

In water:

$$Ag^{3+} + H_2O \rightleftharpoons AgO^+ + 2H^+ \rightleftharpoons Ag^{2+} + H^+ + \frac{1}{2}H_2O_2 \rightleftharpoons Ag^+ + 2H^+ + \frac{1}{2}O_2.$$

The values of activation energy, E, for the decomposition reaction in the two cases have also been calculated and are given by 18,650 cal/mole in acid solution and 27,800 cal/mole in water solution.

In this monograph we have tried to cover references up to the latest publications on the subject, as far as they have been available to us. A glance at the list of references would indicate the wealth of materials accumulated on this topic of a rather limited character. We hope the present review will stimulate further interest in the subject, as there is still ample scope of intensive study on the chemistry of bi- and tripositive silver, particularly in respect of their complex compounds. For, such a study, in our opinion, is likely to reveal many new facts and ideas relating to valency and the structure of chemical compounds, besides elucidating the old ones.

REFERENCES

Austin, P. C. (1911). The interaction of silver nitrate and potassium persulphate and its catalytic effect in the oxidation of organic substances. *J. chem. Soc.*, **99**, 262.

Baborovsky, G. and Kuzma, G. (1909). So-called electrolytic peroxide of silver. *Z. phys. Chem.* **67**, 48.

Bailar Jr., J. C. (1944). Oxidation states of Silver. *J. chem. Educ.*, **21**, 523.

Banerjee, B. and Rây, P. (1956). Complex compounds of bipositive silver with pyridine carboxylic acids, I. Argentic nicotinate and isonicotinate. *J. Indian chem. Soc.*, **33**, 503.

——— (1957). Complex compounds of bipositive silver with pyridine carboxylic acid, II. Argentic compounds of pyridine dicarboxylic acids. *Ibid.*, **34**, 207.

——— (1957). Complex compounds of bipositive silver with pyridine carboxylic acids, III. Argentic compounds of pyridine tricarboxylic acids. *Ibid.*, **34**, 859.

Barbieri, G. A. (1906). Higher forms of combination of silver. *R. C. Accad. Lincei*, **15**, 500.

——— (1907). Bivalent silver. *Ibid.*, **16**, 72.

——— (1912). Argentic persulphate. *Gazz. chim. ital.*, **42**, ii, 7. *R. C. Accad. Lincei*, **21**, 560.

——— (1927). A new salt of bivalent silver. *Ber. dtsch. chem. Ges.*, **B60**, 2424.

——— (1931). Compounds of bi- and tervalent silver. *R. C. Accad. Lincei*, **13**, 882.

(1932). The electrolytic preparation of several complex salts of bivalent silver. *Ibid.*, **16**, 44.

——— (1933). A new type of complex compound of bivalent silver. *Ibid.*, **17**, 1078.

Barbieri, G. A. and Labianca, T. (1954). The use of complexes of bivalent silver with αα'-bipyridyl as an oxidising agent. *Ibid.*, **16**, 88.

Barbieri, G. A. and Malaguti, A. (1950). Higher oxides of silver. *Ibid.*, **8**, 619.

Bawn, C. E. H. and Margerison, D. (1955). Molecular dissociation processes in solution, IV. The rate of decomposition of persulphate ion and its catalysis by metal ions. *Trans. Fararay Soc.*, **51**, 925.

Bekier. E and Kijowski, W. (1934). Catalytic action of silver ions on the velocity of oxidation of manganous salts by persulphate. *Roczn. Chem.*, **14**, 1004.

Berthelot, M. (1880). Action of hydrogen peroxide on silver oxide and metallic silver. *C. R. Acad. Sci., Paris*, **90**, 572.

——— (1880). Silver sesquioxide. *Ibid.*, **90**, 653.

Block, B. P., Bailar Jr., J. C. and Peace, D. W. (1951). The reaction of silver acetate with 8-quinolinol. *J. Amer. chem. Soc.*, **73**, 4971.

Bowers, K. D. (1953). Paramagnetic resonance in an argentic compound. *Proc. phys. Soc. Lond.*, **A66**, 666.

Braekken, H. (1935). Crystal structure of Ag_2O_3. *K. norske vidensk. Selsk. Forh.*, **7**, 143.

Brauner, B. and Kuzma, B. (1907). Separation of heavy metals and the formation of cupric acid. *Ber. dtsch. chem. Ges.*, **40**, 3362.

Brown, M. J. (1916). Silver peroxynitrate. *J. phys. Chem.*, **20**, 680.

Bruno, M. and Santoro, V. (1956). Isotopic exchange reaction between compounds of uni- and bivalent silver. *Ric. sci.*, **26**, 3072.

Burada, A. (1935). Salts of bivalent silver. *Ann. Sci. Univ. Jassy*, **20**, 71.

Capatos, L. and Perakis, N. (1936). Magnetic effect of mixed argentic-cupric crystals. *C. R. Acad. Sci., Paris*, **202**, 1773.

Carman, P. C. (1934). Autoxidation of ammonium persulphate in the presence of silver salts and the trivalent silver. *Trans. Faraday Soc.*, **30**, 566.

Chakraburtty, D. M. and Banerjee, B. (1955). An X-ray study on bivalent silver and copper nicotinate compounds. *Indian J. Phys.*, **29**, 357.

Cox, E. G., Wardlaw, W. and Webster, K. C. (1936). The stereochemistry of quadricovalent atoms : copper and silver. *J. chem. Soc.*, 775.

De Boer, J. H. and Van Ormondt, J. (1952). Proc. International Sym. Reactivity of Solids, Gothenberg, 557.

Dekker, A. O., Levy, H. A. and Yost, D. M. (1937). Reduction of peroxysulphate by manganous ion and by hydrazine with silver ion as catalyst. *J. Amer. chem. Soc.*, **59**, 2129.

Dirkse, T. P. (1959). The silver oxide electrode. *J. electrochem. Soc.*, **106**, 453.

Dirkse, T. P. and Wiers, B. (1959). The stability and solubility of AgO in alkaline solution. *Ibid.*, **106**, 284.

Dutta, R. L. (1955). Studies in less familiar oxidation states, I. Argentic oxide: a new method of prepration. *J. Indian chem. Soc.*, **32**, 95.

Ebert, M. S., Radkowskas, E. L. and Frazer, J. C. W. (1933). Higher valence states of silver. *J. Amer. chem. Soc.*, **55**, 3056.

Fichter, F. and Goldach, A. (1930). Action of fluorine on solutions of silver salts. *Helv. chim. acta*, **13**, 99.

Gordon, B. M. and Wahl, A. C. (1958). Kinetics of the silver(I)-silver(II) exchange reaction. *J. Amer. chem. Soc.*, **80**, 273.

Graff, W. S. and Stadelmaier, H. H. (1958). Higher oxides of silver. *J. electrochem. Soc.*, **105**, 446.

Gruner, E. and Klemm, W. (1937). The magnetic conduct of AgF_2. *Naturwissenschaften*, **25**, 59.

Helmholz, L. and Levine, R. (1942). A determination of parameter in potassium dihydrogen arsenate and silver arsenate. *J. Amer. chem. Soc.*, **64**, 354.

Hieber, W. and Mühlbauer, F. (1928). Complex compounds of bivalent silver (A study on the relation between ring closure and specific affinity). *Ber. dtsch. chem. Ges.*, **B 61**, 2149.

Higson, G. I. (1921). The reaction between persulphate and silver. *J. chem. Soc.*, 2048.

Jirsa, F. (1925). Higher oxides of silver, I. *Z. anorg. chem.*, **148**, 130; *Chem. Listy*, **19**, 3.

——— (1925). Higher oxides of silver, II. Silver peroxide. *Chem. Listy*, **19**, 114, 119, 300.

——— (1947). The reaction of silver nitrate with ammonium peroxysulphate. *Chemie* (Prague), **3**, 4.

——— (1949). Silver oxides, I. Preparation of silver peroxide, Ag_2O_2. *Coll. Trav. Chim. Tchecosl.* **14**, 445.

(1949). Silver oxides, II. Specific heats of silver oxide and peroxide. *Ibid.*, **14**, 451.

Jirsa, F. and Jelinek, J. (1926). The higher oxides of silver, III. Oxidation of silver by ozone. *Z. anorg. chem.*, **158**, 61.

Jirsa, F., Jelineck, J. and Srbek, J. (1926). The higher oxides of silver, II. Silver peroxide. *Ibid.*, **158**, 33.

Jockusch, H. (1934). Silver bifluoride. *Naturwissenschaften*, **22**, 561.

Jones, P. and Thirsk, H. R. (1954). Electrochemical and structural investigation of the process occurring at silver anodes in sulphuric acid. *Trans. Faraday Soc.*, **50**, 732.

Kappana, A. N. and Talaty, E. R. (1951). Electrochemistry of fluoride solution. *J. Indian chem. Soc.*, **28**, 413.

Kleinberg, J. (1950). Unfamiliar Oxidation States and their Stabilization. Univ. of Kansas Press, Lawrence.

Klemm, W. (1931). The magnetism of bivalent silver compounds. *Z. anorg. Chem.*, **201**, 32.

——— (1954). New metallates with coordinated oxygen and fluorine, II. *Angew. Chem.* **66**, 461,

Lingane, J. J. and Davis, D. G. (1956). Argentic oxide as an oxidimetric reagent. Determination of manganese, cerium and chromium. *Anal. Chim. Acta.*, **15**, 201.

Luther, R. and Pokorny, F. (1908). Electrochemical behaviour of silver and its oxides. *Z. anorg. Chem.*, **57**, 290.

McMillan, J. A. (1954). The crystalline structure of AgO. *Acta cryst., Camb.*, **7**, 640.

——— (1960). Magnetic properties and crystalline structure of AgO. *J. inorg. nucl. Chem.*, **13**, 28.

Malaguti, A. (1950). The oxidation of complex ions of univalent silver to complex ions of bivalent silver. *R. C. Accad. Lincei*, **9**, 349.

——— (1952). Reduction of persulphate by hydrogen peroxide. *Ibid.*, **42**, 138.

Malaguti, A. and Labianca, T. (1954). The use of ozone in the preparation of complex salts of bivalent silver. *Gazz. chim. ital.*, **84**, 976.

Malaprade, L. (1940). Isolation of argentiperiodate complexes of trivalent silver. *C. R. Acad. Sci., Paris*, **210**, 504.

Malaprade, L. and Coulombeau, J. (1954). Action of complexes of trivalent silver and of trivalent copper on oxalic acid. *Ibid.*, **238**, 2322.

Malatesta, L. (1941). Salts of trivalent copper and silver, I and II. *Gazz. chim. ital.*, **71**, 467, 580.

Marshall, H. (1900). Action of silver salts on ammonium persulphate solution. *Proc. roy. Soc. Edinb.*, **23**, 163.

Marshall, H. and Inglis, J. K. H. (1902). Action of silver salts on solutions of ammonium persulphate. *Ibid.*, **24**, 88.

Morgan, G. T. and Burstall, F. H. (1930). Research on residual affinity and coordination, XXXII. Complex compounds of bivalent silver. *J. chem. Soc.*, 2594.

——— (1937). Researches on residual affinity and coordination, XXXVII. Complex metallic salts containing 2 :6-Di-2′-pyridyl pyridine (2 :2′ :2″-Tripyridyl). *Ibid.*, 1649.

Morgan, G. T. and Sugden, S. (1931). Paramagnetism of bivalent silver. *Nature, Lond.*, **128**, 31.

Mulder, E. (1897). Silver peroxynitrate. *Rec. Trav. chim. Pays-Bas.*, **16**, 57.

——— (1898). Silver peroxynitrate and silver peroxide. *Ibid.*, **17**, 129.

——— (1900). Silver peroxysulphate and peroxyacetate. *Ibid.*, **19**, 115.

——— (1903). Structural formula of the so-called silver peroxynitrate. *Ibid.*, **22**, 405.

Mulder, E. and Heringa, J. (1896). Silver peroxynitrate. *Ibid.*, **15**, 1, 235.

Nakatsuka, Y. (1936). *Bis*-8-hydroxyquinoline inner complex salt of bivalent silver. *Bull. chem. Soc., Japan*, **11**, 45.

Nakatsuka, Y. and Miwa, T. (1952). A trivalent silver complex compound with oxine. *J. Inst. Polyt., Osaka*, C, **3**, 37.

Neiding, A. B. and Kazarnovskii, A. (1951). Nature of the higher silver oxide. *C. R. Acad. Sci. U.R.S.S.*, **78**, 713.

Noyes, A. A., Coryell, C. D., Stitt, F. and Kossiakoff, A. (1937). Argentic salts in acid solution, IV. The kinetics of the reduction by water and formation by ozone of argentic silver in nitric acid solution. *J. Amer. chem. Soc.*, **59**, 1316.

Noyts, A. A., Devault, D., Coryell, C. D. and Deahl, T. J. (1937). Argentic salts in acid solution, V. Oxidation potentials, equilibria with higher silver oxides and formation of nitrate complexes. *Ibid.*, **59**, 1326.

Noyes, A. A., Hoard, J. L. and Pitzer, K. S. (1935). Argentic salts in acid solution, I. The oxidation and reduction reactions. *Ibid.*, **57**, 1221.

Noyes, A. A., and Kossiakoff, A. (1935). Argentic salts in acid solutions, III. Oxidation potentials of argentous-argentic salts in nitric acid solution. *Ibid.*, **57**, 1238.

Noyes, A. A., Pitzer, K. S. and Dunn, C. L. (1935). Argentic salts in acid solutions, II. The oxidation states of argentic salts. *Ibid.*, **57**, 1229.

Orgel, L. E. (1956). Tenth Solvay Conference in Chemistry, Brussels, p. 320.

Pauling, L. (1945). Nature of the Chemical Bond. Cornell Univ. Press.

Perakis, N. and Capatos, L. (1938). Thermomagnetic study of the silver-cadmium and copper-cadmium system. *J. Phys. Radium*, **9**, 27.

Parakis, N. and Capatos, L. (1939). The magneto-chemistry of solid solutions. *Ibid.*, **10**, 234.

Râv, P. (1946). The Theory of Valency and the Structure of Chemical Compounds. Indian Ascociation for the Cultivation of Science, Calcutta.

Rây, P. and Chakravarty, K. (1944). Complex compounds of biguanide with tervalent metals, XI. Silver (Ag^{111}) ethylenedibiguanide and its salts. *J. Indian chem. Soc.*, **21**, 47.

Rây, P. and Sarma, B. (1948). Magneto-chemical studies in valency, IV. Tetrapositive nickel as nickel periodates. *Ibid.*, **25**, 205.

Rây P. and Sen, D. N. (1948). Magneto-chemical studies in valency, VI. Bond type and stereochemistry of four-coordinated copper complexes. *Ibid.*, **25**, 473.

Ritter (1804). *Gehlen's Neus J.*, **3**, 561.

Rochow, E. G. and Kukin, I. (1952). The use of chlorine trifluoride as a fluorinating agent. *J. Amer. chem. Soc.*, **74**, 1615.

Ruff, O. and Giese, M. (1934). The fluorination of silver and copper. *Z. anorg. Chem.*, **219**, 143.

Scatturin, V., Bellon, P. L. and Zannetti, R. (1958). Planar coordination of the group IB elements: crystal structure of Ag(II) oxide. *J. inorg. nucl. Chem.*, **8**, 462 ; *Ric. sci.*, **27**, 2163 (1957).

Schiel, J. (1864). An experiment for demonstration. *Liebigs Ann.*, **132**, 322.

Schwab, G. M. and Hartman, G. (1955). Silver (II) oxide. *Z. anorg. Chem.*, **281**, 183.

Scrocco, E. and Marmani, G. (1954). Temperature coefficient of the oxidation-reduction potential of uni- and bivalent silver complexes with dipyridyl. *R. C. Accad. Lincei*, **16**, 637.

Scrocco, E., Marmani, G. and Mirone, P. (1950). Oxidation-reduction potential of complexes of univalent and bivalent silver. *Bull. Sci. facolta chim. ind. Bologna*, **8**, 119.

Scrocco, E. and Ragazzini, M. (1954). Uni- and bivalent silver complexes with phenonthroline. *R. C. Accad. Lincei*, **16**, 489.

Sen, B. N. (1948). On some physico-chemical evidences of the divalency of silver. *Curr. Sci.*, **17**, 182.

Sen, D. (1960). Unpublished work.

Sen, D., Ghosh, N. N. and Rây, P. (1950). Physico-chemical studies on the stability of ethylenedibiguanide complex of tripositive silver. *J. Indian chem. Soc.*, **27**, 619.

Sen, D. and Rây, P. (1953). A study on the decomposition of tripositive silver complex : silver ethylenedibiguanide nitrate. *Ibid.*, **30**, 519.

Sone, K. (1949). The colour of complex compounds of bivalent silver. *J. chem. Soc. Japan*, Pure Chem. Sec., **70**, 63.

Sugden, S. (1932). Magnetism and valency, I. Copper and silver compounds. *J. chem. Soc.*, 161.

Sulc, O. (1896). So-called electrolytic silver peroxide (silver peroxynitrate). *Z. anorg. Chem.*, **12**, 89 ; (1900), **24**, 305.

Tanaka, M. (1954). Use of silver peroxide in the volumetric and colorimetric determination of vanadium. *Bull. chem. Soc., Japan*, **27**, 10.

Tanatar, S. L. (1901). The so-called silver peroxynitrate. *Z. anorg. Chem.*, **28**, 331.

Wartenberg, H. V. (1939). Heat of formation of AgF_2. *Ibid.*, **242**, 406.

Watson, E. R. (1906) Silver dioxide and silver peroxynitrate. *J. chem. Soc.*, **89**, 578.

Weber, H. C. P. (1917). Silver peroxide and valency of silver. *Trans. Amer electrochem. Soc.*, **32**, 391.

Wöhler, F. (1867). On the preparation of silver peroxide with ozone. *Liebigs Ann.*, **146**, 263.

Yost, D. M. (1926). Catalysis by silver ion of the oxidation of chromic salts by persulphuric acid. The existence of trivalent silver compound. *J. Amer. chem. Soc.*, **48**, 152.

——— (1926). The catalytic effect of silver ammonia ion in the oxidation of ammonia by persulphate. *Ibid.*, **48**, 374.

Yost, D. M. and Claussen, W. H. (1931). Reduction of peroxysulphate by vanadyl ion with silver ion as catalyst. *Ibid.*, **53**, 3349.